Experimental Heat Capacities of Nitrogen-Hydrogen Sulfide Mixtures at Elevated Pressures

Gerald P. Hamaliuk,[1] P. Raj Bishnoi, and Donald B. Robinson[2]
University of Alberta, Edmonton, Alta., Canada

The ratio of the heat capacity at a pressure to the heat capacity at a low pressure was measured experimentally for two mixtures of gases, one containing 91.4 mol % nitrogen and 8.6 mol % hydrogen sulfide and the other containing 76.5 mol % nitrogen, 22.2 mol % hydrogen sulfide, and 1.3 mol % carbon dioxide. Data were obtained at temperatures of 40.0°, 60.1°, and 90.1°C at pressures up to 2350 psia. The measurements are believed to be accurate to ±0.5%. Heat capacities for the two mixtures predicted by the ideal heat capacity equations and the BWR equation with new mixing rules agreed well with the experimental measurements. The maximum deviation was 2.6% at 2300 psia and 40.0°C for the mixture containing 22.2% hydrogen sulfide.

Thermodynamic data have long played an important role in process calculations and design. Over the years, considerable effort has been expended in improving and developing more precise design procedures, but in the final analysis, any of these methods is limited by the availability and reliability of the data. The methods used for making these calculations have frequently been based on experimental PVT data of fluids and their ideal gas properties. Values for thermal and other derived properties obtained in this way are subject to uncertainties because they involve first and sometimes second-density derivatives. This is one of the reasons why in recent years there has been an increased interest in the direct experimental determination of properties such as enthalpy and specific heats.

An additional motivation for experimental work of this kind is that the development and improvement of more advanced predicting and correlating procedures require accurate independent data on at least some representative systems.

Hydrogen sulfide, nitrogen, and carbon dioxide are present in varying quantities in many natural gases. Experimental data on the enthalpy or heat capacity of gases containing carbon dioxide or hydrogen sulfide are almost completely lacking; however, recently the heat capacities at elevated pressures of the carbon dioxide-methane and carbon dioxide-nitrogen systems have been reported (*2*, *3*). As a continuation of this program, work was undertaken to experimentally determine the heat capacities of hydrogen sulfide-nitrogen mixtures over a range of temperatures and at pressures up to 2350 psi. The data were obtained for two binary mixtures containing 8.60 and 22.2% hydrogen sulfide at temperatures of about 40°, 60°, and 90°C. A comparison of the experimentally obtained data was then made with the values predicted by the Benedict-Webb-Rubin (*1*) (BWR) equation of state by use of the new mixing rules recently formulated by Bishnoi and Robinson (*4*).

Experimental

The experimental method used in this work was based on an idea which was originally suggested by Burnett (*8*) and later used by Workman (*11*). In this method a heat exchanger is used as a calorimeter. The high-pressure gas at a given temperature is passed through the heat exchanger, and the pressure of this stream is then dropped outside the exchanger to some lower value, at which the heat capacity of the gas is either known or can be calculated reliably. The temperature of this low-pressure stream is adjusted to a suitable level. The gas is then passed through the calorimeter where it exchanges heat with the high-pressure stream. Thus, the high and low-pressure streams have the same mass flow rates.

The first law of thermodynamics when applied to this calorimeter at steady state reduces to:

$$H_1 - H_2 + H_3 - H_4 \pm Q/F = 0 \qquad (1)$$

where H refers to the specific enthalpy of the flowing fluid. Locations 1 and 3 refer to the inlet, and locations 2 and 4 refer to the outlet of the high and low-pressure streams, respectively. Q is the rate of heat leak to and from the exchanger, and F is the mass flow rate of the fluid.

The only observations required when using this method are the inlet and outlet temperatures and pressures of the two streams. Measurement of energy transfer is not required, and the mass flow rate need not be measured accurately.

If the pressure and temperature changes of the high and low-pressure streams passing through the exchanger are small, Equation 1 reduces to either 2 or 3, depending upon whether the high-pressure gas is being cooled or heated.

$$\frac{C_p}{C_{p_o}} = \left|\frac{\Delta T_o}{\Delta T}\right| + \phi\,(\mu, C_p, \mu_o, C_{p_o}, q) \qquad (2)$$

$$\frac{C_p}{C_{p_o}} = \left|\frac{\Delta T_o}{\Delta T}\right| - \phi'\,(\mu, C_p, \mu_o, C_{p_o}, q) \qquad (3)$$

If the absolute temperature levels of the heat exchanger are not very different for the two cases of heating and cooling the high-pressure gas, the terms ϕ and ϕ' are of the same order of magnitude. Thus, if a series of experiments is conducted over a desired pressure range to obtain one set of data for heating the high-pressure gas and another set for cooling it, two curves may be obtained by plotting $\Delta T_o/\Delta T$ vs. pressure. The separation between these curves is related to ϕ or ϕ', both of which are dependent upon correction terms such as heat leak, Joule-Thomson effect of the gas owing to pressure drop in the exchanger, and the temperature measurement errors. The character as well as the position of the two curves can point out imperfections of the apparatus. For example, if the calorimeter is properly designed, the upper and lower curves when extrapolated should pass symmetrically about unity at a pressure equal to that of the low-pressure stream. A curve obtained by averaging the upper and lower curves should give the dependence of $C_p/C_{p(o)}$ ratio on pressure at a constant temperature. The average curve, when extrapolated to a pressure equal to that of the low-pressure stream, should pass through

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[1] Present address, Mobil Oil Canada Ltd., Calgary, Alta., Canada.
[2] To whom correspondence should be addressed.

unity. Moreover, the $C_p/C_{p(o)}$ ratios thus obtained will be independent of the errors usually associated with calorimetry.

From the foregoing, the errors involved in determinations made by the heat exchanger method are not only evident from the nature and position of the two curves, but $C_p/C_{p(o)}$ ratios can be obtained which are independent of these errors. The validity of the data obtained may be immediately checked by extrapolating the average curve to a pressure equal to that of the low-pressure stream.

The absolute value of the heat capacity at a high pressure can be found if the heat capacity at the low pressure is known. The low-pressure heat capacity can be calculated by applying a small correction to the zero-pressure heat capacity. The zero-pressure heat capacity for a simple molecule can be calculated from statistical thermodynamics with an accuracy equal to or better than the measured values. The low-pressure heat capacity can then be calculated from the zero-pressure heat capacity by using a suitable equation of state for the fluid.

Materials and Analysis

The nitrogen used in the present work was obtained from a local supplier and was stated to have a purity of 99.993 mol %. A sample of this nitrogen was analyzed on a silica gel column, and no impurity peaks were detected. Hydrogen sulfide (C.P. grade) was obtained from Matheson Inc., and contained about 4% carbon dioxide in the vapor phase. After two distillations, the carbon dioxide content in the vapor was reduced to approximately 3%. To avoid any heavier impurities, the vapor from the cylinder was withdrawn and condensed into a separate chamber, and the condensed liquid was subjected to two or more single-stage distillations. The liquid was then used to prepare the two mixtures with nitrogen for which the experimental data were obtained.

The gas chromatograph used for analyzing the hydrogen sulfide and the two mixtures was a Hewlett-Packard Model 700 equipped with a thermal conductivity cell and a 3-ft long, ⅛-in. diameter poropack QS column maintained at 60°C. The chromatograph was calibrated by use of the pure components hydrogen sulfide, nitrogen, and carbon dioxide, thus establishing the response curve for each component. Generally, the analyses were repeatable to within ±0.2 mol %, and enough samples were taken to gain an accuracy of about the same value. The analyses of the two mixtures for which the heat capacity data were obtained are reported below in mole fractions:

	N_2	H_2S	CO_2
Mixture I	0.914	0.086	Trace
Mixture II	0.765	0.222	0.013

Apparatus

A schematic representation of the experimental apparatus is given in Figure 1. A detailed description of the calorimeter and the auxiliary equipment has been given elsewhere by Bishnoi and Robinson (*6*).

Results and Discussion

Two sets of experiments were carried out for each isotherm, one for cooling and one for heating the high-pressure fluid. For every data point, ΔT_o (low-pressure tem-

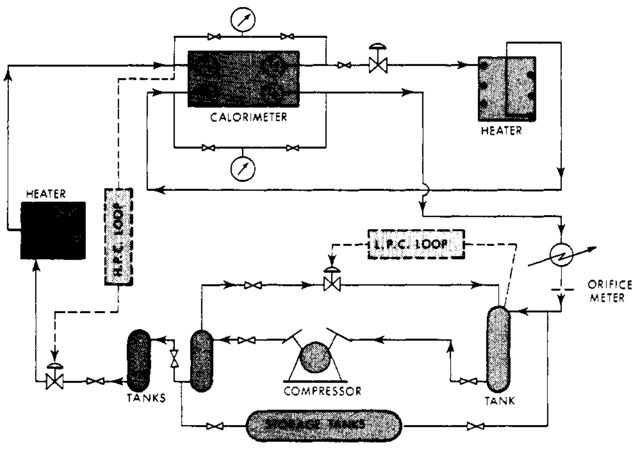

Figure 1. Schematic flow sheet of experimental equipment

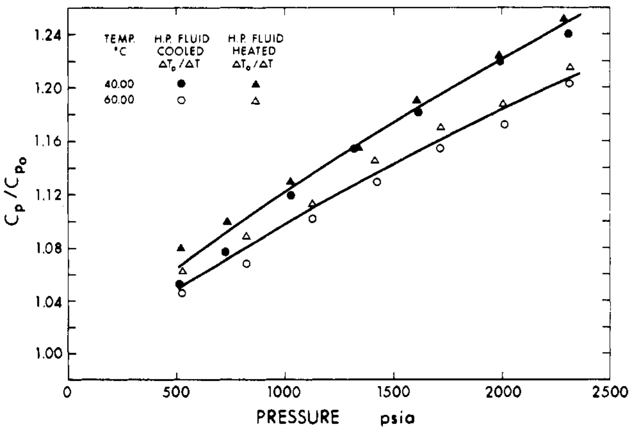

Figure 2. Ratio of heat capacity at pressure to heat capacity at low pressure for mixture containing 8.6 mol % hydrogen sulfide

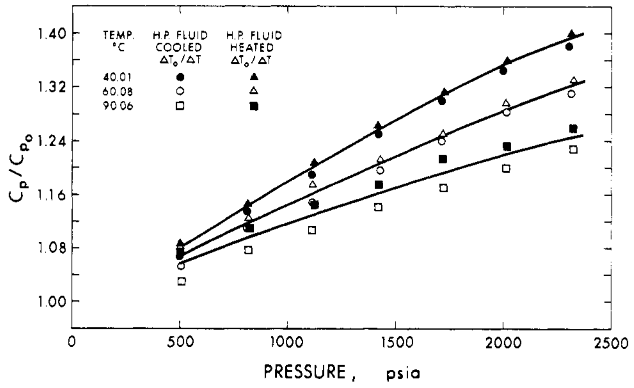

Figure 3. Ratio of heat capacity at pressure to heat capacity at low pressure for mixture containing 22.2 mol % hydrogen sulfide, 76.5 mol % nitrogen, and 1.3 mol % carbon dioxide

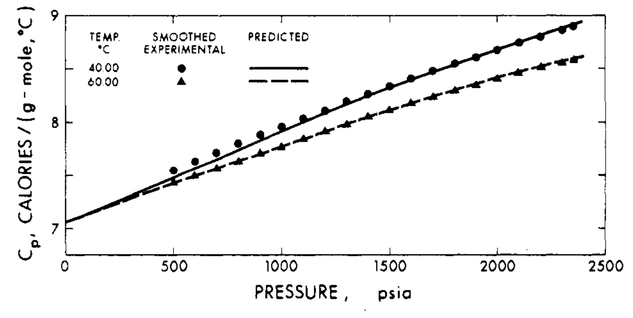

Figure 4. Comparison of experimental heat capacities of mixture containing 8.6 mol % hydrogen sulfide with values predicted by BWR equation

perature change) and ΔT (high-pressure temperature change) were observed every minute during a steady state period of about 30 min. Temperature probe corrections were applied to the observed ΔT_0 and ΔT, and the corresponding $\Delta T_0/\Delta T$ was calculated. These ratios were then averaged, and the average $\Delta T_0/\Delta T$ was corrected to the "isotherm" temperature. The isotherm temperature was obtained by taking an average of the inlet and outlet high-pressure gas temperatures for all the data points of an isotherm. This was necessary because the average temperatures of the high and low-pressure streams for a data point were slightly different than the isotherm temperature. The corrected $\Delta T_0/\Delta T$ ratios thus obtained for the two sets for each isotherm were smoothed separately by the least-squares criterion of fit. All data sets were smoothed by the Forsyth polynomial (*9*) since higher degree polynomials were not required. In the smoothing process for the data sets, a weight inversely proportional to the square of the root mean square deviation was assigned to each point.

The smoothed values of the $\Delta T_0/\Delta T$ ratios for the two cases of heating and cooling the high-pressure gas for

Table I. Smoothed Values of C_p/C_{p_0} for Mixture I

Isotherm temp, °C	40.00	60.00
Low pressure, psia	28.5	28.8
Low-pressure heat capacity (C_{p_0}), cal/g-mol K	7.093	7.098
p, psia	C_p/C_{p_0}	C_p/C_{p_0}
500	1.065	1.048
550	1.071	1.053
600	1.077	1.058
650	1.082	1.063
700	1.088	1.069
750	1.094	1.074
800	1.100	1.079
850	1.105	1.084
900	1.111	1.089
950	1.117	1.094
1000	1.122	1.098
1050	1.128	1.103
1100	1.133	1.108
1150	1.138	1.113
1200	1.144	1.117
1250	1.149	1.122
1300	1.154	1.126
1350	1.160	1.131
1400	1.165	1.136
1450	1.170	1.140
1500	1.175	1.144
1550	1.180	1.148
1600	1.185	1.153
1650	1.190	1.157
1700	1.195	1.161
1750	1.200	1.165
1800	1.204	1.169
1850	1.209	1.173
1900	1.214	1.177
1950	1.218	1.181
2000	1.223	1.185
2050	1.228	1.189
2100	1.232	1.193
2150	1.236	1.196
2200	1.241	1.200
2250	1.245	1.204
2300	1.250	1.207
2350	1.254	1.211

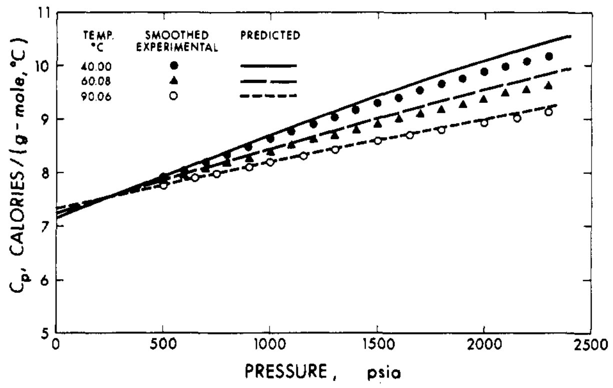

Figure 5. Comparison of experimental heat capacities of mixture containing 22.2 mol % hydrogen sulfide with values predicted by BWR equation

Table II. Smoothed Values of C_p/C_{p_0} for Mixture II

Isotherm temp, °C	40.01	60.08	90.06
Low pressure, psia	28.7	28.7	28.5
Low-pressure heat capacity (C_{p_0}), cal/g-mol K	7.306	7.318	7.344
p, psia	C_p/C_{p_0}	C_p/C_{p_0}	C_p/C_{p_0}
500	1.080	1.068	1.057
550	1.091	1.076	1.063
600	1.101	1.084	1.069
650	1.111	1.092	1.075
700	1.122	1.100	1.081
750	1.132	1.108	1.087
800	1.142	1.115	1.093
850	1.151	1.123	1.099
900	1.161	1.131	1.105
950	1.171	1.138	1.111
1000	1.180	1.146	1.116
1050	1.190	1.153	1.122
1100	1.199	1.160	1.128
1150	1.208	1.168	1.133
1200	1.218	1.175	1.139
1250	1.227	1.182	1.144
1300	1.236	1.190	1.150
1350	1.245	1.197	1.155
1400	1.254	1.204	1.160
1450	1.262	1.211	1.166
1500	1.271	1.218	1.171
1550	1.280	1.225	1.176
1600	1.288	1.231	1.181
1650	1.296	1.238	1.186
1700	1.305	1.245	1.191
1750	1.313	1.252	1.196
1800	1.321	1.258	1.200
1850	1.329	1.265	1.205
1900	1.336	1.271	1.210
1950	1.344	1.278	1.214
2000	1.351	1.284	1.218
2050	1.358	1.290	1.223
2100	1.365	1.297	1.227
2150	1.372	1.303	1.231
2200	1.379	1.309	1.235
2250	1.385	1.315	1.239
2300	1.391	1.321	1.243
2350	1.397	1.327	1.247

each isotherm were generated at equal intervals of 50 psi, and their average was calculated. The average values thus calculated are equal to the heat capacity ratios. Heat capacity ratios thus determined for the two mixtures are presented graphically in Figures 2 and 3. For the sake of clarity, the average values are shown as curves, and the experimental values of the temperature corrected $\Delta T_o/\Delta T$ ratios are shown as points.

The low-pressure heat capacity of the nitrogen-hydrogen sulfide mixtures at various isotherm temperatures was calculated from the BWR equation of state and the ideal gas heat capacity equations for nitrogen and hydrogen sulfide (*10*). The low-pressure heat capacities and the heat capacity ratios at various temperatures for the two mixtures reported in Tables I and II are expected to be accurate within ±0.5%. Heat capacities calculated from the experimental heat capacity ratios would have additional errors owing to the polynomial approximations of the ideal gas heat capacities and the calculations of the low-pressure heat capacities from the ideal gas values. It is, however, expected that these errors would be negligibly small compared to the experimental errors.

Comparison with Values Calculated from BWR Equation of State

The heat capacities of nitrogen-hydrogen sulfide mixtures were predicted at the temperatures and compositions corresponding to the data obtained in this work and at pressures up to 2400 psia with an interval of 50 psi. The calculations were performed by use of the ideal gas heat capacity equations for nitrogen, hydrogen sulfide, and carbon dioxide (*10*), the BWR equation of state (*4*), and the new mixing rules referred to earlier. The values of the binary interaction parameters used with these rules were taken as 0.068 for nitrogen-hydrogen sulfide, 0.057 for carbon dioxide-hydrogen sulfide, and 0.03 for carbon dioxide-nitrogen. BWR coefficients for carbon dioxide, hydrogen sulfide, and nitrogen were taken from Bishnoi and Robinson (*4, 5*) and Bloomer and Rao (*7*), respectively.

A comparison of the predicted heat capacities with the experimental data was made graphically and is shown in Figures 4 and 5 for the two mixtures. The largest deviations of the experimental data occurred at 40.01°C for the mixture containing 22.2 mol % hydrogen sulfide. The maximum of these deviations was about 2.6% at the highest pressure of 2300 psia. Generally, the predictions deviated from the experimental data by less than 1.5%, and the predictions for the mixture containing 8.6 mol % hydrogen sulfide at 60°C had the smallest errors.

Conclusions

The heat exchanger method of determining the ratio of heat capacity at a pressure to the heat capacity at a low pressure was used to obtain data on two mixtures of hydrogen sulfide and nitrogen containing 8.6 and 22.2 mol % hydrogen sulfide. The data were obtained in the temperature range of ambient to 90°C at pressures to 2350 psia with an accuracy of ±0.5%.

Heat capacities of the two mixtures were predicted by use of the ideal gas heat capacity equations for hydrogen sulfide and nitrogen, together with the BWR equation and the new mixing rules. Comparison of the predicted values with the experimental data showed that the predictions correctly reproduced the trend of the experimental data. In general, most of the predictions deviated from the experimental data within less than 1.5%, with the maximum deviation being 2.6% at 2300 psia and 40.01°C for the mixture containing 22.2% hydrogen sulfide.

Nomenclature

C = heat capacity
F = mass flow rate of calorimeter fluid
H = specific enthalpy of flowing fluid
ϕ, ϕ' = mathematical functions
q = rate of heat transfer to or from exchanger per unit of mass flow
Q = total rate of heat transfer to or from exchanger
T = absolute temperature
μ = Joule-Thomson coefficient

Subscripts

1, 2, 3, 4 = specific locations in the exchanger
o = constant low pressure
p = any constant pressure

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